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Preparation of Copper Aluminium Oxide by Spray Pyrolysis

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ABSTRACT

Copper aluminium oxide(CuAlO_2) particles, a promising p-type TCO(transparent conducting oxide), were prepared by spray pyrolysis. Delafossite phase of CuAlO_2 was obtained when copper nitrate, copper acetate and copper sulfate, divalent copper precursors, were used as copper precursor and aluminium nitrate as aluminium precursors. However, when copper chloride (CuCl , a monovalent copper precursor) was used, the delafossite phase was not obtained regardless of the type of aluminium precursor. The O_2 -doped CuAlO_2 was obtained by using oxygen as carrier gas.

INTRODUCTION

The CuAlO_2 particles are prepared by solid-state reactions of Cu_2O and Al_2O_3 . [1] Solid-state reaction method is cheap and oxide precursors are readily available. But this method needs repeated milling and calcination, and the prepared particles have irregular morphology and large size. The spray pyrolysis has some advantages in comparison to the solid-state reaction method. Spray pyrolysis is simple and has the ability to produce chemically homogeneous multi-metal oxides[2]. A wide variety of reactants can be used as long as they have proper solvent. This flexibility allows the use of inexpensive reactants such as metal nitrates, chlorides, fluorides, etc.

In this work, copper aluminium oxide particles with delafossite were prepared by the spray pyrolysis for the first time. Various metal salts were used as precursors, and their effects on the crystal structure were investigated. The bulk conductivity of CuAlO_2 is known to be 1.7×10^{-3} S/cm [3] and the origin of positive hole in CuAlO_2 is not clear but may be excess oxygen[4]. To obtain higher conductivity, M. S. Lee et al. annealed CuAlO_2 pellet at 943 K under O_2 atmosphere for O_2 doping to CuAlO_2 . However, the doping process decomposed CuAlO_2 into CuO and CuAl_2O_4 [5]. Therefore, the particles were prepared by using oxygen as carrier gas to prepare O_2 doped CuAlO_2 .

EXPERIMENTAL DETAILS

The spray pyrolysis system consisted of an ultrasonic nebulizer and a reaction furnace. The stock solution was atomized with a sonicator equipped with 1.7 MHz resonator. Copper nitrate, copper acetate, copper sulfate (divalent copper precursors) and copper chloride (a monovalent copper precursor) were tested as copper precursors and aluminium nitrate, aluminium chloride and aluminium sulfate were tested as aluminium precursors. Stock solutions of 0.5 M were prepared by dissolving copper and aluminium precursors into two different solvents. Copper chloride was dissolved into 15 wt.% HCl because of its low solubility in pure water and the other precursors were dissolved in distilled water. The reactor temperature was fixed at 973 K. The flow rate of carrier gas was 4 L/min. Air, N_2 and O_2 were used as carrier gas. The as-prepared

particles were annealed at 1073, 1373 and 1573 K for 3 hours for crystallization. The crystalline structure was characterized by x-ray diffraction(XRD). The conductivity was measured by the 4-probe method at room temperature. For measurement of conductivity, pellets of 13mm in diameter and 0.2mm in thickness were fabricated by pressing at 3000 psia. As a reference, conductivity of particles which were prepared by solid-state reaction at 1373K for 10hr was measured by the same method.

RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of particles prepared from copper nitrate and aluminium nitrate. The particles had different peaks depending on annealing temperatures. Before annealing, they had only CuO peaks. The particles annealed at 973 K had peaks of CuO and CuAlO₂ which was not a TCO(transparent conducting oxide). After annealing at 1373 K, they were converted to CuAlO₂ of delafossite structure. Being annealed at 1573 K, the particles had peaks corresponding to CuO, Cu₂O and Al₂O₃. It is clear that there exists an optimum post-treatment temperature. In this experiment, samples treated at 1373 K, give the delafossite structure.

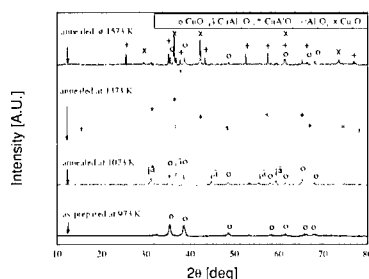


Figure 1. The XRD spectra of particles prepared from starting solution of Cu(NO₃)₂ and Al(NO₃)₃ after annealing at 973, 1373 and 1573 K. [carrier gas : air]

Figure 2 shows the effect of the types of copper and aluminium precursor. Figure 2(a) is the XRD pattern of particles prepared from aluminium nitrate. When copper nitrate, copper acetate and copper sulfate were used as copper precursor, the particles had delafossite phase. The particles prepared from copper chloride(CuCl) which was a monovalent copper precursor had not only delafossites (CuAlO₂) but also spinel phase(CuAl₂O₄). But spinel peaks were stronger than delafossite peaks. Therefore, copper chloride was not a suitable copper precursor. The result is contradictory to the solid state reaction in which only monovalent copper precursor is suitable for the formation of delafossite phase.

Figure 2(b) is the XRD patterns of particles prepared by using aluminium chloride. In this case, the delafossite phase was obtained from copper nitrate and copper sulfate. But they had spinel phase, too. The particles prepared from copper acetate and copper chloride had peaks of CuAl₂O₄ and Al₂O₃. Therefore, aluminium chloride is not suitable for preparing pure delafossite phase

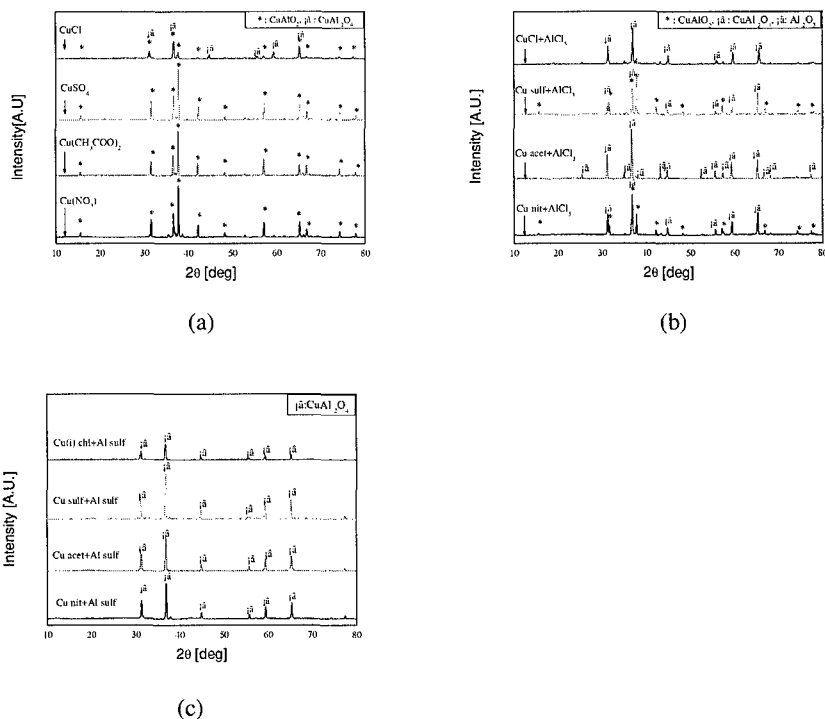


Figure 2. The XRD spectra of particles prepared from aluminium nitrate(a), aluminium chloride(b) and aluminium sulfate(c) after annealing at 1373K.[carrier gas : air]

Figure 2(c) is the XRD spectra of particles prepared from aluminium sulfate. The particles prepared by using aluminium sulfate had not delafossite structure but spinel phase of CuAl_2O_4 regardless of the types of copper precursors.

Figure 3 shows that the kind of carrier gas did not affect crystal structure of particles. The particles were prepared from stock solution of copper nitrate and aluminium nitrate and had delafossite structure after annealing at 1373K regardless of carrier gas. The conductivity was affected by carrier gas. The conductivities of particles are in table 1. The pellet of the particles prepared by using O_2 as carrier gas had the highest conductivity. It shows that using O_2 as carrier gas help to prepare O_2 doped copper aluminate.

Table 1. Conductivities of particles.

Precursors	Cu nit + Al nit			Cu acet+Al nit	Cu sulf+Al nit	Solid-state reaction
	N_2	Air	O_2	Air	Air	
Conductivity[S/cm]	0.205	0.157	0.589	0.138	0.015	0.376

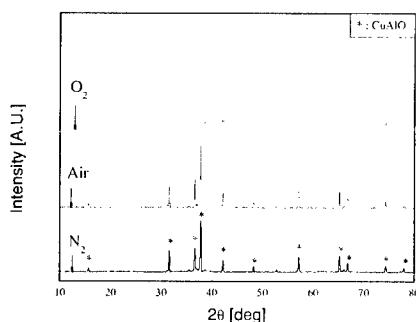


Figure 3. The XRD spectra of particles prepared by using O_2 , air and N_2 as carrier gas and annealed at 1373 K. [copper precursor : $Cu(NO_3)_2$, aluminium precursor : $Al(NO_3)_3$]

CONCLUSIONS.

Copper aluminium oxide particles with delafossite were prepared by spray pyrolysis for the first time. $Cu(NO_3)_2$, $Cu(CH_3COO)_2$ and $Cu(SO_4)$ can be used as copper precursor. However, only $Al(NO_3)_3$ was a proper aluminium precursor. For doping oxygen, O_2 had to be used as carrier gas. In the solid-state reaction, post-treatment with O_2 converted the $CuAlO_2$ to $CuAl_2O_4$ and CuO . Therefore, it was expected that O_2 doped $CuAlO_2$ was difficult to be prepared by solid-state reaction. The highest conductivity was achieved when $Cu(NO_3)_2$ and $Al(NO_3)_3$ was used as precursors, and O_2 as carrier gas. This value was higher than the bulk conductivity of $CuAlO_2$ prepared by solid-state reaction.

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